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Optimization of Atmospheric Air Plasma for Degradation of Organic Dyes in Wastewater

Chaitanya Sarangapani
Technological University Dublin, chaitu.s.304@gmail.com

Yash Dixit
Technological University Dublin

Vladimir Milosavljevic
Technological University Dublin

Carl Sullivan
Technological University Dublin, carl.sullivan@tudublin.ie

Paula Bourke
Technological University Dublin, paula.bourke@tudublin.ie

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Corresponding Author:	chaitanya sarangapani IRELAND
Corresponding Author Secondary Information:	
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First Author:	chaitanya sarangapani
First Author Secondary Information:	
Order of Authors:	chaitanya sarangapani
	yash dixit
	paula bourke
	carl sullivan
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Optimization of atmospheric air plasma for degradation of organic dyes in wastewater

Chaitanya Sarangapani[1], Y. Dixit[1], Vladimir Milosavljevic, Paula Bourke[1], Carl Sullivan[1], P.J. Cullen[1,2]

[1]BioPlasma Research Group, Dublin Institute of Technology, Dublin 1, Ireland

[2]School of Chemical Engineering, University of New South Wales, Sydney, Australia.

*Corresponding Author (✉): P.J. Cullen; Tel (☎): +353 1 402 7595; E-Mail: pjcullen@dit.ie

Abstract:

This study optimises the degradation of cocktail of dyes methyl orange and bromothymol blue by atmospheric air plasma. Response Surface Methodology (RSM) was employed to investigate the efficacy of the plasma process parameters on degradation efficiency. A Box Behnken Design (BBD) was employed to optimise the degradation of dyes by air plasma discharge. A second order polynomial equation was proposed to predict process efficiency. It was observed that the predicted values are significant ($p<0.001$) with coefficients of determination 0.98, 0.96, 0.98 for dye degradation, pH value and ozone concentration respectively. The ANOVA results showed that the coefficients of the polynomials for the percentage degradation and ozone concentration responses indicated positive linear effects ($p<0.001$) whereas a negative linear effect was found for pH. The positive linear effect of variable emphasises that voltage and treatment time were the most dominant factors ($p<0.001$) meaning that higher degradation efficiencies are achieved with increase in treatment duration. This study showed that a BBD model and response surface methodology could be employed to optimize the colour degradation parameters of non-thermal plasma treated model dyes while minimising the number of experiments required.

Keywords: Atmospheric air plasma, Methyl orange, bromothymol blue, RSM.

1. Introduction:

Atmospheric air cold plasma is an emerging advanced oxidation process (AOP) for the treatment of organic contaminants. Such plasma discharges have recently been proposed for medical applications such as sterilization, bio-decontamination, surface modification and for environmental applications such as air pollution and as surface engineering tool (Machala *et al.* 2007; Sarangapani *et al.* 2016b). In a recent study, Jiang et al.,(2014) reviewed the application of non-thermal or cold plasma for the treatment of waste water. The unique and highly active chemistry associated with atmospheric plasmas offer significant potential for the degradation of contaminants in water and wastewater (Mok *et al.* 2008). Dielectric Barrier Discharge (DBD) plasma discharges initiates several physical processes viz., UV light, shock waves and chemical processes viz , ·OH, ·O, ·H, radicals, ozone and hydrogen peroxide which directly or indirectly lead to the degradation of organic compounds (Sarangapani *et al.* 2015; Thirumdas *et al.* 2015). In addition to this, positive and negative ions, excited species, excited neutral molecules are also generated. The mechanism of degradation initiates with the formation of high energy electrons in the discharge (Rohit Thirumdas 2016). These high energy electrons react with gas and water molecules to produce reactive species like ·O,·H, ·OH, O_3 (Feng *et al.* 2008). Metastables such as ozone are highly soluble in water and forms ·OH (Wei *et al.* 2014), however the efficacy of UV radiation is found to be reduced in the presence of O_3. A number of studies have demonstrated the successful degradation of organic dyes using DBDs. Reports on the degradation of azo dyes include methylene blue (Reddy *et al.* 2013) and methyl orange (Grabowski *et al.* 2007) degradation. Non-thermal plasma technology in combination with modified activated carbon fibers was also used for the degradation of organic dyes (Jiang *et al.* 2013). It has been observed from previous study (Misra *et al.* 2015) that the efficiency of non-thermal dye degradation is

dependent on various parameters such as applied voltage, treatment time, initial dye concentration, pH and ozone. In order to study a process, conventional methods and classical methods were used. In this methods, the influence of each of these parameters were carried out by varying studied parameters while keeping others constant (Kasiri *et al.* 2013). These methods are also time consuming, requires a number of experiments to determine optimum levels, which are unreliable. Moreover, these methods do not depict the combined effect of all parameters involved. These limitations can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) (Ravikumar *et al.* 2007). RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing the processes. This is technique can also estimate linear, interaction, and quadratic effects of the factors and provides a prediction model for the response. In fact, this can also be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions with minimum number of experiments.(Ravikumar *et al.* 2007). Hence, this method can be applied for optimizing the atmospheric plasma process parameters for degradation of dyes. Few reports on use of RSM in optimization of decolorisation process by advanced oxidation processes include comparable studies on optimization using RSM include the degradation of azo dyes by ozonation (Muthukumar *et al.* 2004; Kasiri *et al.* 2013) and the degradation of Reactive Green 19 (RG19) by the UV/H_2O_2 treatment(Zuorro *et al.* 2013). Such approaches help minimise the number of experiments required for process optimisation. Also, to facilitate industrial adoption of this technology an improved understanding of treatment efficiency and the efficacy of plasma process parameters optimization on the degradation of dyes is required. Moreover, to the best of

our knowledge there are no studies on the optimization of non-thermal process parameters for the degradation process as an emerging Advanced oxidation process (AOP).

In this study, modelling and optimization of dye degradation for a cocktail of analytical grade methyl orange and bromothymol blue was performed by employing box-behnken design with RSM methodology. The study employs the use of a high voltage, large gap DBD plasma with atmospheric air as the inducer gas, which has recently shown significantly higher efficacies for dye degradation (Misra *et al.* 2015), pesticide degradation (Moiseev *et al.* 2014) and microbial inactivation (Patil *et al.* 2014) than studies previously reported at lower voltages. Given the low energy input and use of atmospheric air, the process has potential for large scale waste water treatment applications. The influencing factors (variables) employed were voltage, treatment time and dye concentration. Responses monitored were the degradation efficiency, ozone concentration and pH.

2. Materials and Methods:

2.1. Materials

2.1.1Reagents and selection of dye concentration

Analytical-grade methyl orange and bromothymol blue dyes were obtained (Sigma-Aldrich, Ireland). Concentrations of these dyes were prepared by serial dilution to a final concentration within the maximum absorption range of the UV-Vis spectrophotometer (Shimadzu UV 1800, Shimadzu Scientific Instruments). Based on the spectral data of the dilutions, a cocktail of the three dye standards was prepared in water at 50mg/L, 75 mg/L and 100mg/L concentration each

2.1.2Atmospheric air plasma treatment:

The experimental set-up employed for this work is shown in **Fig 1**. The apparatus consists of two aluminium plate electrodes of circular geometry (outer diameter = 158 mm) which are covered with dielectric materials of 2 mm thickness for ground electrode and 10mm thick perspex for high voltage electrode. In between the two dielectrics recide a removable polypropylene (PP) reactor of dimensions 310 mm × 230 mm × 22 mm. Each reactor holds a petri plate with 10 ml dye placed directly between the electrodes. The reactor acts as a closed chamber holding the reactive species generated and as an additional dielectric. In order to prevent loss of the reactive species generated during and after treatment, the PP containers with petri plate were sealed inside a high barrier Cryovac BB3050 film. An additional layer of PP board was placed at the ground electrode in order to prevent arcing and distribute the discharge uniformly. Atmospheric air was used as a working gas. The top electrode was connected to a high voltage step-up transformer (Phenix Technologies, Inc., USA) where the primary winding receives input at 230 V, 50 Hz and delivers a high voltage output in the range 0-120 kV $_{RMS}$. Plasma treatment was performed at different voltages (30-80kV) and treatment times (30-180 seconds). Treatment of all dye samples was carried out in duplicate and at ambient temperature (16-18 ℃). All sealed containers were then kept at room temperature of 16-18℃ for a post treatment storage time of 24 h to ensure contact with longer lived species.

2.2. Experimental design and Data analysis:

The effect of the three independent process parameters; voltage X_1(kV), treatment time X_2(sec) and dye concentration X_3(mg/L) on the dependent variable were studied using response surface methodology. A box-behnken design was employed, and coded as -1, 0, 1 with the ranges determined via preliminary studies. The independent variables were X_1 (30-70kV$_{RMS}$), X_2 (30-

180 s), X_3 (50-100mg/L). The experimental data was randomised and the total 15 experiments were carried out. The experimental design in the actual and the coded values (-1, 0, 1) of variables is shown in **Table 1**. Data analysis, experimental design and regression modelling were done using statistical software R (R Core Team). A second order polynomial model was fitted to the experimental data obtained from the box-behnken design. BBDs are very efficient as they reduce experimental runs in comparison to central composite design (CCD). The design does not contain any points at the vertices of the cubic region and therefore the design points fall within a safe operating limit i.e.within the nominal high and low levels (Anuar *et al.* 2013).

$$Y = b_0 + \sum_{i=1}^{2} b_i X_i + \sum_{i=1}^{2} b_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} b_{ij} X_i X_j \qquad (1)$$

Where Y is the predicted response, b_0 is the constant (intercept), b_i is the linear coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the cross product coefficient, X_i and X_j are the independent variables

2.3. Electrical characterisation of discharge

Electrical characterisation of the discharge was performed using an Agilent InfiniVision 2000 X-Series Oscilloscope (Agilent Technologies Inc., USA). The voltage across the electrode was recorded using a high voltage North Star PVM-6 probe together with a 10:1 voltage divider. The current waveform was measured using a current transformer probe (Bergoz CT-E1.0S).

2.4. Ozone measurement

Ozone concentrations generated within the reactor were taken as a measure of one of the meta stable oxygen species generated and measured using short-term ozone detection tubes obtained from Gastec (Product No. 18M, Gastec, Japan). These tubes contain a reagent which changes its colour upon contact with the specified gas and are calibrated for specific sampling volumes.

Ozone concentrations were measured immediately following each treatment. Further details regarding gas measurement methodology can be found elsewhere (Misra *et al.* 2014).

2.5. Optical emission spectroscopy

Spectra of the discharge emissions were acquired with a computer controlled Ocean Optics spectrometer (HR2000+), to which the light from the plasma is coupled via an optical fibre (**Fig 1**). The fibre had a numerical aperture of 0.22 and is optimised for use in the ultraviolet and visible portion of the spectrum. The HC1 variable blaze diffraction grating coupled with a 25 μm slit allows for a wavelength resolution of 1.1 nm. The spectrometer operates in the wavelength range of 200 nm to 1050 nm. Emission spectra and corresponding noise spectra were recorded using integration times of 5000 ms and averaged over 10 measurements. Spectra were recorded with and without dye samples in the reactor during the discharge. All spectra were corrected for noise levels by subtracting the background noise.

2.6. Absorption spectra of dyes

The dye samples were sampled into 1 cm path length cuvettes and their visible absorption spectra were obtained using a spectrophotometer (Shimadzu UV 1800, Shimadzu Scientific Instruments). Degradation efficiency was defined as the percentage decrease of absorbance according to the following equation

$$Degradation\,[\%] = \frac{A_0 - A}{A_0} \times 100 \qquad (2)$$

Where A_0 is the absorbance of untreated dye solution (0s treatment) and A is the absorbance at time‘t’ at wavelength of maximum absorption (λ_{max}).

A first-order kinetics model was evaluated for modelling the experimental data for dye degradation. The first-order model is given by equation 3:

$$A_t = A_{max} - A_{max} e^{-kt}, A_{max} \leq 100 \quad (3)$$

Where, A_t is the % degradation at any time, t (s), A_{max} is the maximum degradation, k is the rate constant (s^{-1})

2.7. Measurement of pH

The pH of all dye samples were measured after 24h storage using a calibrated glass electrode ORION pH meter (model 420A, Thermo Fisher Scientific Inc.) at ambient temperature (16 ℃).

3. Results and discussion:

3.1. Preliminary analysis of dye degradation:

The absorption spectrum of the dyes is shown in **Fig 2**. The maximum absorption was observed in the visible region (λ_{max}=616 nm). The degradation process was investigated by observing the respective spectral changes. However, it was observed that a decline in the intensities at two wavelengths, in the UV (λ_{max} = 308 nm) and visible (λ_{max}= 616,624 nm) regions were associated with an increase in the treatment time. The decrease in intensities was due to degradation and dearomatization of organic dye by plasma excited and reactive species $O^{\bullet}$,$^{\bullet}OH$, $N^{\bullet}$, $HO_2^{\bullet}$, N_2*, N*, OH^-, O_2^-, O^-, O_2^+, N_2^+, N^+, and O^+ (Dojčinović *et al.* 2011). **Fi.2.** shows the absorbance changes at 616 nm as a function of time for a treatment at voltage 40kV. The % degradation increased with treatment time and the degradation process followed first-order kinetics with the rate constant increasing with treatment time. The results obtained from preliminary analysis concluded that increase in treatment time increases degradation efficiency. The increase in

plasma input parameters of voltage increases the generation of reactive species such as ozone, hydroxyl radicals, and hydrogen peroxide.

3.2. Current-Voltage characteristic of plasma source:

The typical waveforms found for the discharge at different voltages are shown in **Fig. 3**. A stable non-thermal discharge was seen at large gaps of 2.3 cm. The observations deduced that the applied voltage was sinusoidal and the total current in the dielectric barrier discharge consists of filamentary streamers which may trigger photo ionization. The dielectric material plays a key role in the operation by limiting the charge and preventing arcing (Dojčinović *et al.* 2011). Further details regarding electrical characteristics of the discharge using capacitance-voltage Lissajous patterns can be found in a recent publication by (Moiseev *et al.* 2014).

3.3. Optical Emission Spectroscopy (OES) of plasma:

The energy transferred to the plasma causes excitation of the air molecules. Optical emission spectroscopy was employed to identify the chemical species formed by the plasma. The spectrum of radiations emitted was grated and OES intensities were measured as a function of wavelength. The emission spectrum obtained in the wavelength range of 180-900 nm for atmospheric air plasma at 50 and 70 kV with and without samples are shown in **Fig.4**. The emissions were stronger for the empty containers than those containing samples; which was due to the influence of the samples on the discharge area. The spectral reading was recorded within a few seconds of plasma initiation.

It is evident from the emission spectrum (300-400 nm) that the DBD operating in atmospheric air is a weak source of UV, which is in agreement with the previous studies conducted by (Heise *et al.* 2004). The distinct peaks observed in the UV region are emissions from N_2 and excited

species of N_2^+ (Pearse *et al.* 1976). Small peaks related to OH were found near 295-300 nm and low emissions of O were also noted between 780 and 840 nm (Laux *et al.* 2003). The lower intensities of these emissions were expected in the air plasmas due to quenching of O (^{3}P) and O (^{5}P) (Walsh *et al.* (2010). It could be inferred from the spectra, that the atmospheric air plasma employed is a source of reactive oxygen and nitrogen species (ROS & RNS).

3.4. Second order polynomial model

In this experiment, a box behnken design was used to form a mathematical model for the degradation process behaviour. The experiments were performed according to the design, factors and the selected levels. The coefficients of the mathematical model were estimated to predict the response and finally, the adequacy of the generated model was determined. The box behnken design (BBD) matrix showing coded and actual level of variables are presented in **Table 2**. The experimental and predicted results of the response functions (% degradation, pH value and ozone concentration) are presented in **Table 3**.

The second order polynomial (equation 1) was used to correlate the dependent and independent variables. The value of the coefficients was estimated using ANOVA (**Table 4**) and the second-order equation used for predicting the response functions (% degradation, pH value and ozone concentration) for methyl orange dye is expressed as follows (equations 4-6):

$$(\%degradation)Y = 91.674 + 6.289x_1 + 5.400x_2 - 0.685x_3 - 2.852x_1x_2 - 0.019x_1x_3 + 0.096x_2x_3 + 1.531x_1^2 - 1.675x_2^2 - 0.947x_3^2 \quad (4)$$

$$(pHvalue)Y = 2.757 - 0.090x_1 - 0.100x_2 + 0.020x_3 - 0.01x_{(1)}x_2 - 1.138\times10^{-16}x_1x_3 + 0.015x_2x_3 + 0.064x_1^2 - 0.083\times10^{-2}x_2^2 - 0.004x_3^2 \quad (5)$$

$$(Ozoneconc.)Y = 1650 + 525x_1 + 506.250x_2 - 31.250x_3 + 125x_1x_2 + 25x_1x_3 - 62.500x_2x_3 - 231.250x_1^2 - 93.750x_2^2 + 156.25x_3^2 \quad (6)$$

The response functions viz. % degradation, pH value and ozone concentration were predicted by equations 4,5 and 6 respectively and the values are shown in **Table 4**.

3.5. Model validation

Fig.5. shows the predicted values of the response functions; % degradation, pH value and ozone concentration. The coefficient of determination (R^2) shows the accuracy of the predicted models. It is evident from **Fig.6.**, that the models were able to predict the response functions with high accuracy indicated by high R^2 values of 0.98, 0.96, and 0.98 for % degradation, pH value and ozone concentration respectively. The model explains about 98%, 96%, and 98% variability of the response functions; % degradation, pH value and ozone concentration respectively.

3.6. Fitting the quadratic model using Analysis of variance

Analysis of variance (ANOVA) was used to test the significance and capability of the model. The results of the quadratic response surface model fitting in the form of analysis of variance are shown in **Table 4**. The proposed models predicted the performance of the plasma process on the basis of following response functions; % degradation, pH value and ozone concentration with high accuracy as evident from the R^2 values. Adjusted R^2 is a better measure of the goodness of fit as compared to R^2 for comparing models with different numbers of independent variables (Kasiri *et al.* 2013). In the present study, adjusted R^2 values and the corresponding R^2 values were close to each other as shown in **Table 4**.

The F ratio is the ratio between the mean square of the model and the residual error. It shows whether the model is significant or not when compared to their respective residual errors. If the *F* value is greater than the tabulated value of the *F* distribution for a certain number of degrees of freedom in the model at the level of significance α, then the model is a good predictor of the experimental results (Kasiri *et al.* 2013). The *F* values for % degradation, pH value and ozone concentration were 27.21, 12.25, and 29.52 respectively, which were greater than the tabulated *F* values (4.772 at 95% significance) confirming the adequacy of the model fits.

3.7. Analysis of box behnken design results using surface and contour plots

The Student's *t* test determines the significance of the regression coefficient of the parameters. The *P* values also check the significance of each of the coefficients and are necessary to understand the mutual interactions between the test variables (Kasiri *et al.* 2013). The surface plots were generated keeping one variable constant at their zero level and the other two variables varied within their experimental range. These plots represent the linear as well as quadratic effects of the individual variables.

The coefficients of polynomials relating to the % degradation of the dye indicate that the linear effects of the variables were prominent except for the dye concentration (**Table 4**). Applied voltage had the strongest positive linear effect (**Fig. 6 a, b**) which was followed by the treatment time (**Fig. 6 b, c**). The % degradation observed was maximum at the highest voltage and longest treatment duration. The quadratic effects of these variables were usually non-significant (at $p=0.10$) except for the interaction effect of voltage and treatment time which was significant (at $p\leq0.05$) and produces a negative effect. This means that the effect of voltage on the % degradation depends on the duration of treatment time. This phenomenon produces a curvilinear effect on the % degradation (**Fig.6. a**). If the experiments were conducted by

conventional methods, the significance of quadratic and interaction effects between variables would have been lost. Chemically, the degradation of the dye was due to cleavage of the azo groups (-N= N-) which are responsible for the characteristic colour of the dye. Irreversible discoloration of the dye was due to oxidative species in a particular ozone and hydroxyl radicals which break the aromatic and other molecules containing –C=C- and -N= N- bonds. Oxidation takes place either due to direct or indirect oxidative reactions by converting to hydroxyl radical (Huang *et al.* 2010).

Error! Reference source not found. shows the coefficients of polynomials for pH values, where it was observed that the negative linear effect of treatment time was the most dominant factor (**Fig. 7 a, c**) which means that an increase in the treatment time increases the acidity of dye. The shift in pH values in the dye samples after plasma treatment may be due to the formation of strong acids like nitric acid (HNO_3) and nitrous acid (HNO_2) as well as due to hydrogen peroxide (H_2O_2) (Oehmigen *et al.* 2010). Diffusion of active species into the solution with oxidation of the dyes was responsible for the acid formation. The next factor of importance was voltage which also had a negative linear effect on pH ($p \leq 0.01$). The quadratic effect of voltage alone was significant (at $p \leq 0.05$), which produces a curvilinear effect on pH (**Fig.7.a, b**). The quadratic effect of the other variables was non-significant.

$$N_2 + e^- \rightarrow 2N^{\bullet} + e^- \quad (7)$$

$$O_2 + e^- \rightarrow 2O^{\bullet} + e^- \quad (8)$$

$$N^{\bullet} + O^{\bullet} \rightarrow NO_2 \quad (9)$$

$$NO_2^- + H_2O_2 + H_3O^+ \rightarrow ONOOH + 2H_2O \quad (10)$$

$$ONOOH + 2H_2O \leftrightarrow ONOO^- + H_3O^+ \quad (11)$$

$$NO_2 + OH^- \rightarrow HNO_3 \quad (12)$$

The coefficients of polynomials (**Table 4**) indicate that the linear effects of the variables related to the ozone concentration were prominent. Among all three variables, voltage had the strongest positive linear effect (**Fig. 8. a, b**) which was followed by the positive linear effect due to treatment time (**Fig. 8. a, c**). However, the effect due to dye concentration was non-significant. High dye concentration logically enhances the probability of collision between organic matter and oxidizing species, leading to a decrease in the discoloration rate. The quadratic effects of these variables were non-significant except for voltage alone (significant at $p \leq 0.05$). It produces a curvilinear effect on ozone concentration (**Fig. 8 a, b**). The following mechanism explains the formation of ozone equations 13-15.

$$e + O_2 \rightarrow O + O + e \quad (13)$$

$$O + O_2 \rightarrow O_3 \quad (14)$$

$$3O_3 + H_2O \rightarrow 2 . OH + 4O_2 \quad (15)$$

Dielectric barrier discharge (DBD) is one of the most efficient methods to produce ozone (Amjad *et al.* 2012). Ozone which is produced in DBD acts as a powerful oxidant with a redox potential of 2.07 which is also chemically stable (Tizaoui & Grima 2011). Using high voltage permits an increased number of collisions with oxygen to form ozone. Ozone mechanism of degradation proceeds in two stages, firstly molecular interactions through electrophillic attack on

bonds such as –N=N– azo chromophoric groups, double bonds of –C=C– connecting aromatic groups. Secondly, oxidation of dye is subject to direct reaction with compounds such as –OH, –CH_3, –OCH_3, –NH_2 and attack on atoms such as N, P, O, S (Am Water Works Res *et al.* 1991; Maciejewska *et al.* 2000). Several authors have reported the mechanism of degradation by ozone takes place indirectly at high pH, while in acidic environments direct reaction is predominant (Misra *et al.* 2015; Sarangapani *et al.* 2016a). At low pH a slow reaction takes place between the dissolved ozone and hydrogen peroxide which result in the formation of hydroxyl radicals, but these reactions are greatly accelerated at high pH. Thus, ozone, hydroxyl radicals, hydrogen peroxide are considered as the principal active species responsible for the degradation of dyes (see equations16-23). Besides ozone, electrical discharges in humid air also produce a variety of excited and active species, such as $O^{\bullet}$, $^{\bullet}OH$, $N^{\bullet}$, $HO_2^{\bullet}$, N_2*, N*, OH^-, O_2^-, O^-, O_2^+, N_2^+, N^+, and O^+ (Dojčinović *et al.* 2011). Ozone and other active species produced in the gas phase subsequently gets dissolved in the aqueous phase and reacts with the dye. For a detailed computational analysis of the principal meta stable species generated with this DBD ACP system the reader is directed to (Moiseev *et al.* 2014).

$$H_2O + e^- \rightarrow H^{\cdot} + OH^{\cdot} + e^- \quad (136)$$

$$O + O_2 \rightarrow O_3 \quad (17)$$

$$H_2O + e^- \rightarrow H^{\cdot} + OH^{\cdot} + e^- \quad (18)$$

$$O_3 + {}^{\cdot}OH \rightarrow {}^{\cdot}HO_2 + O_2 \quad (19)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad (20)$$

$$H^{\cdot} + O_2 \rightarrow HO_2 \quad (21)$$

$$HO_2^{\cdot} + H^{\cdot} \rightarrow H_2O_2 \quad (22)$$

$$H_2O_2 + O_3 \rightarrow .OH + O_2 + .HO_2 \quad (23)$$

The results from ANOVA suggests that second order polynomials can adequately explain all three response functions. Further, among the independent variables, the voltage has the most dominant positive linear effect on the % degradation and ozone concentration. However, it had a negative linear effect on pH. The second most dominating effect was treatment time which also possesses similar effects on all three response functions as voltage. However, dye concentration does not seem to have any effect on the response functions. All the independent variables except dye concentration mostly offer a linear effect while their quadratic and interaction effects were marginal. A high coefficient of determination (R^2= 0.98, $p \leq 0.001$), (R^2= 0.96, $p \leq 0.01$) and (R^2= 0.98, $p \leq 0.001$) indicates the suitability of the second order polynomial for the % degradation, pH value and ozone concentration respectively. The accuracy of the predicted models was determined by performing paired t-test among experimental and predicted values. The optimized conditions of plasma process parameters for maximum degradation and ozone concentrations were found to be 70kV voltage, 120s treatment time and100mg/L dye concentration. The results of paired t-test showed that the values were not significant at p<0.05 and predicted values were within range of experimental values.

3.8. Conclusion

It can be concluded that response surface methodology (RSM) using box–behnken (BBD) design is an effective technique to investigate colour degradation for the cocktail of dyes as a function of the plasma process parameters. RSM could effectively predict and optimise the plasma

process. Results from analysis of variance showed high coefficient of determination values (R^2>0.95) for the three responses ensuring a satisfactory adjustment of the second-order polynomial model with the experimental data. The significant influence either independently or interactively, on degradation by the three independent variables were clearly described through response surface plots. Plasma process parameters; treatment time and voltage were found to be most significant factors for degradation. The findings in particular demonstrate the potential impact of employing very high voltages (>70 kV) on the degradation efficacy of air plasmas for wastewater treatment. This study improved understanding of the effect of plasma on degradation of colour which is one of the critical parameters of wastewater. However, these results indicate the feasibility of atmospheric air plasma as an emerging technology for industrial adoption.

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Figures

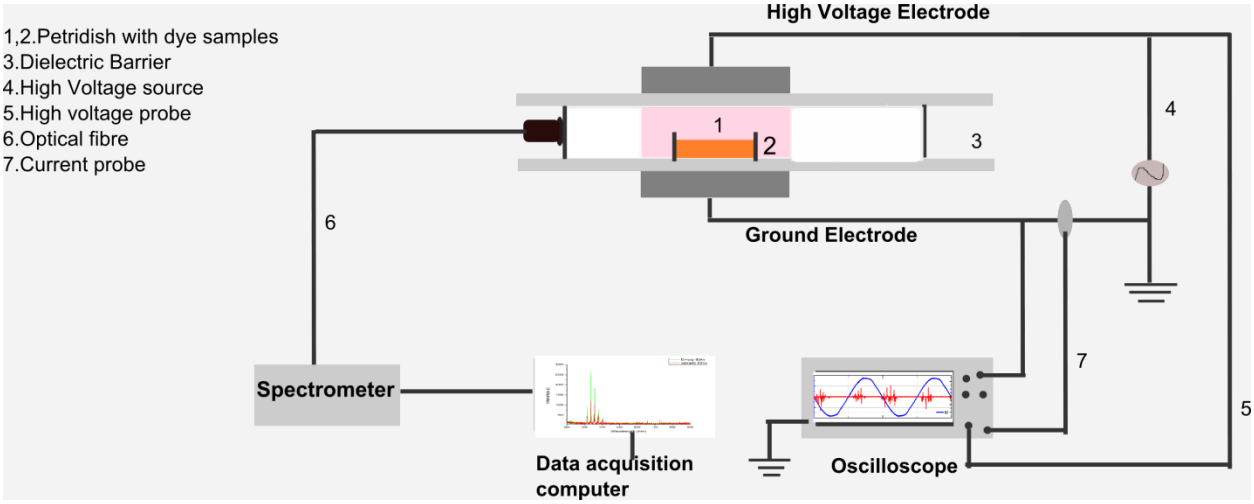


Fig.1. Schematic of the experimental setup with electrical and optical diagnostics

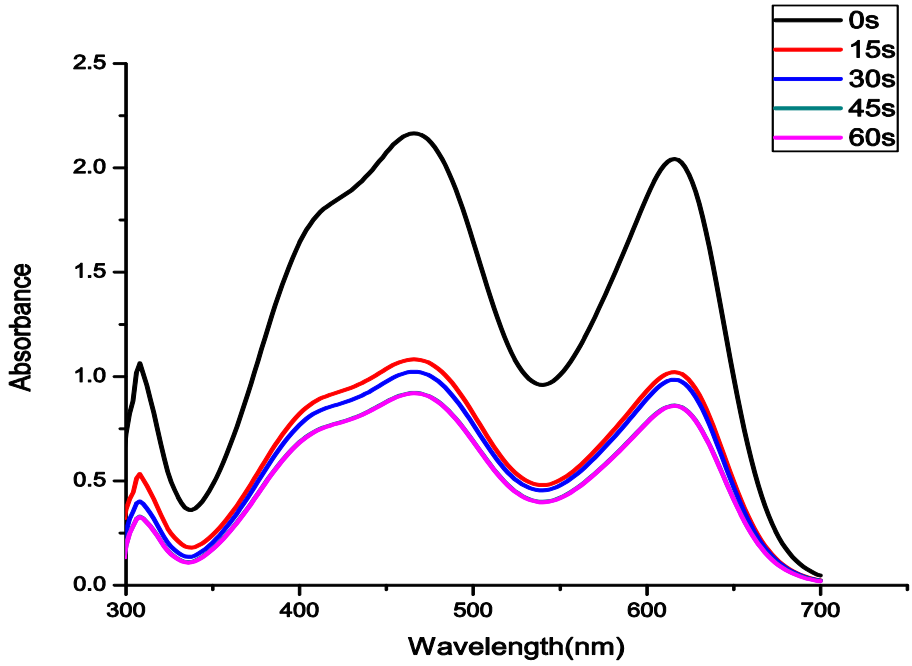


Fig.2. Absorption spectra of dye mixture treated directly at 40kVRMS across the electrodes, after 24h storage

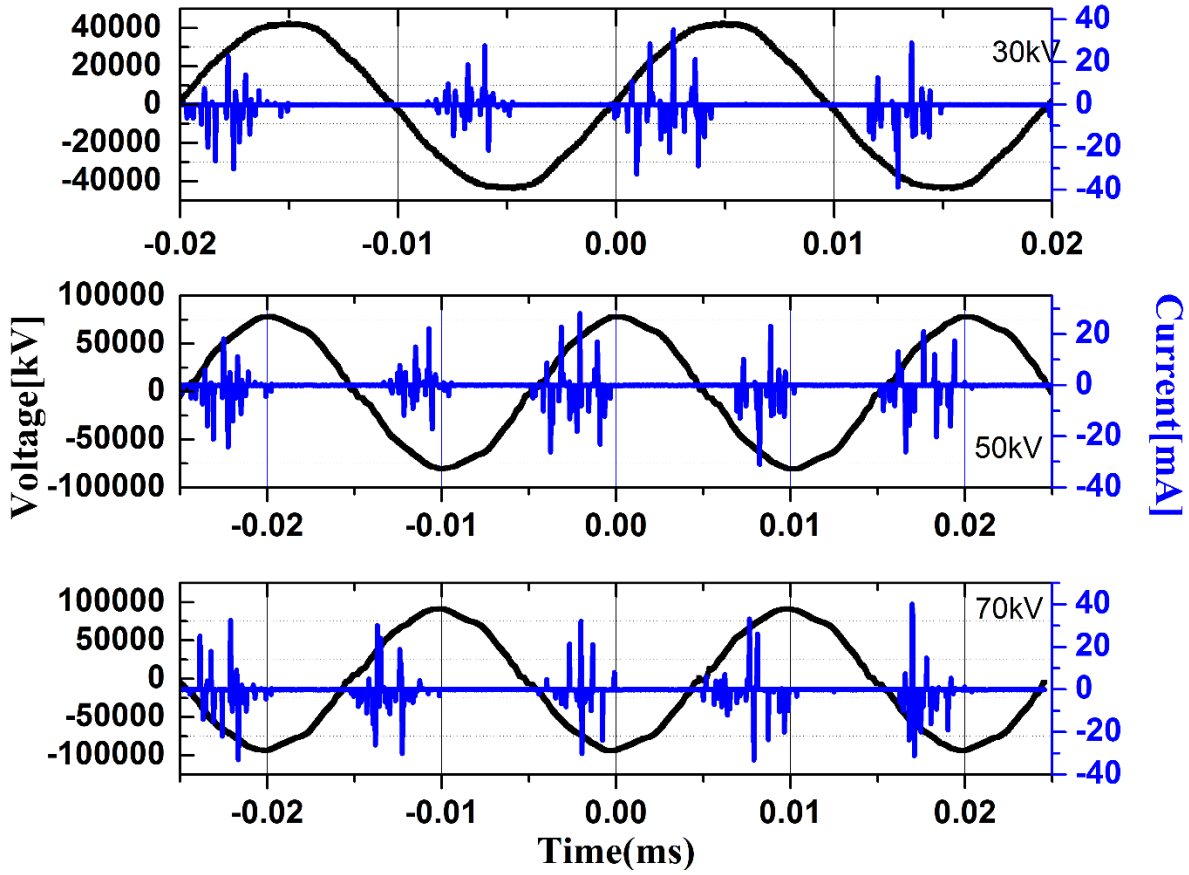


Fig.3. Representative I-V waveforms of the discharge in packages

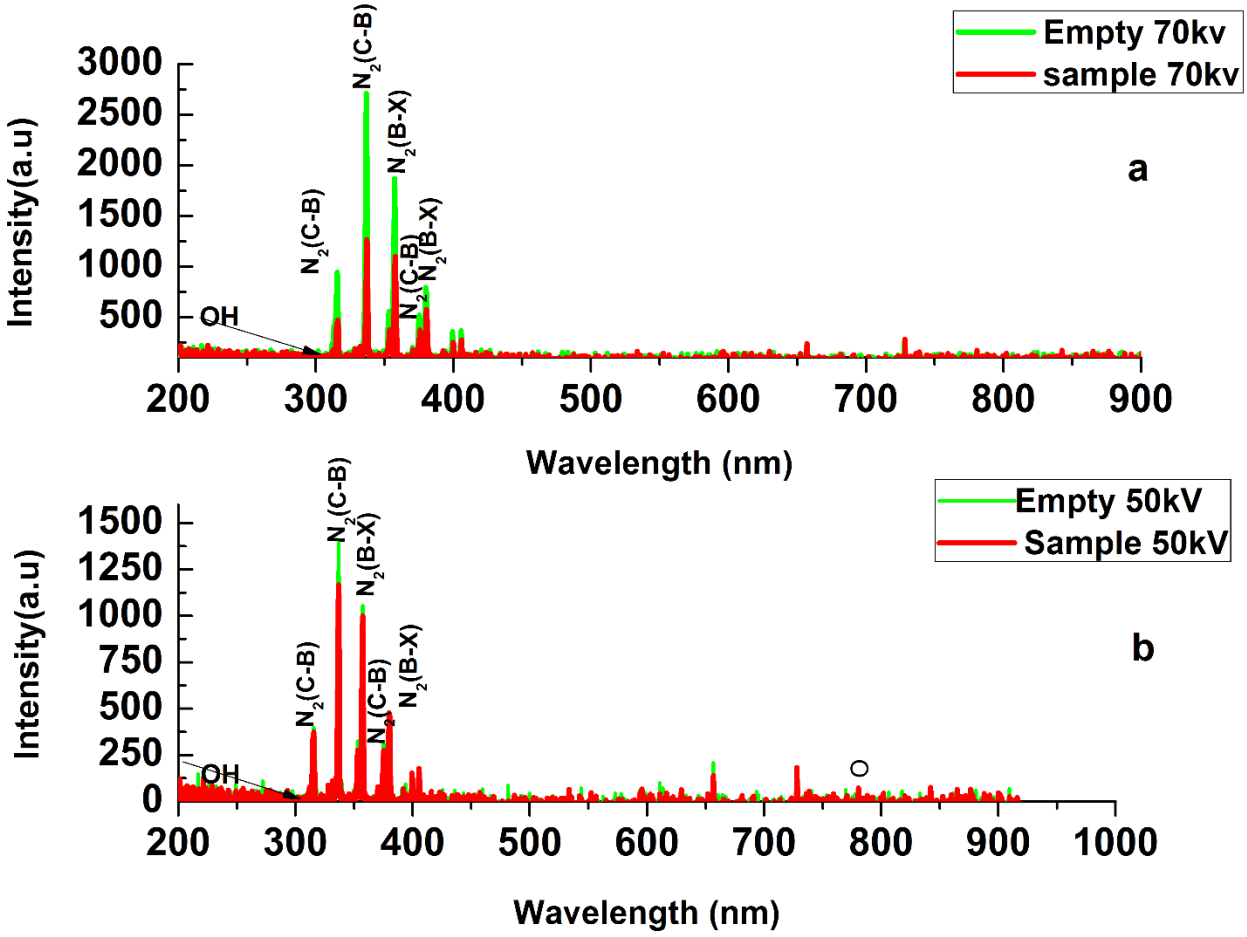


Fig.4. Typical Optical Emission Spectrum (OES) of the dielectric barrier discharge in air.

Operating voltage, a) 50 and b) 70 kV (RMS)

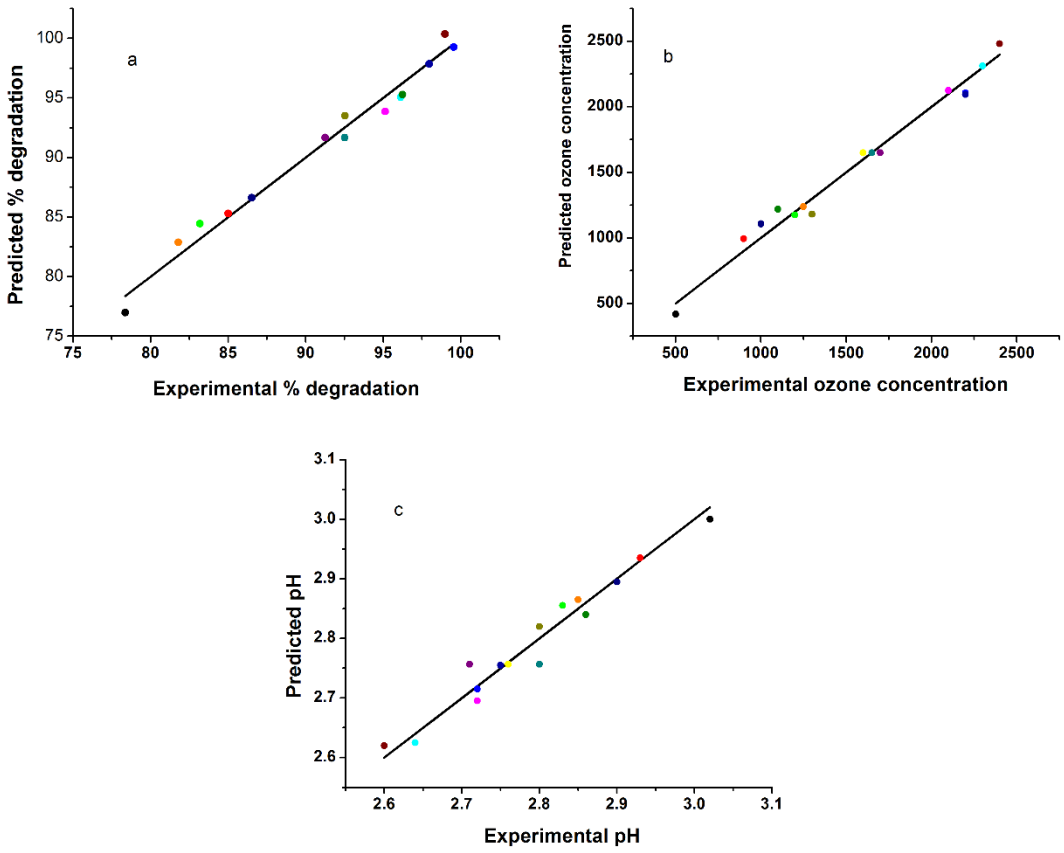


Fig.5. Correlation between predicted and experimental values for each of the degradation parameters studied a) % degradation b) ozone concentration c) pH

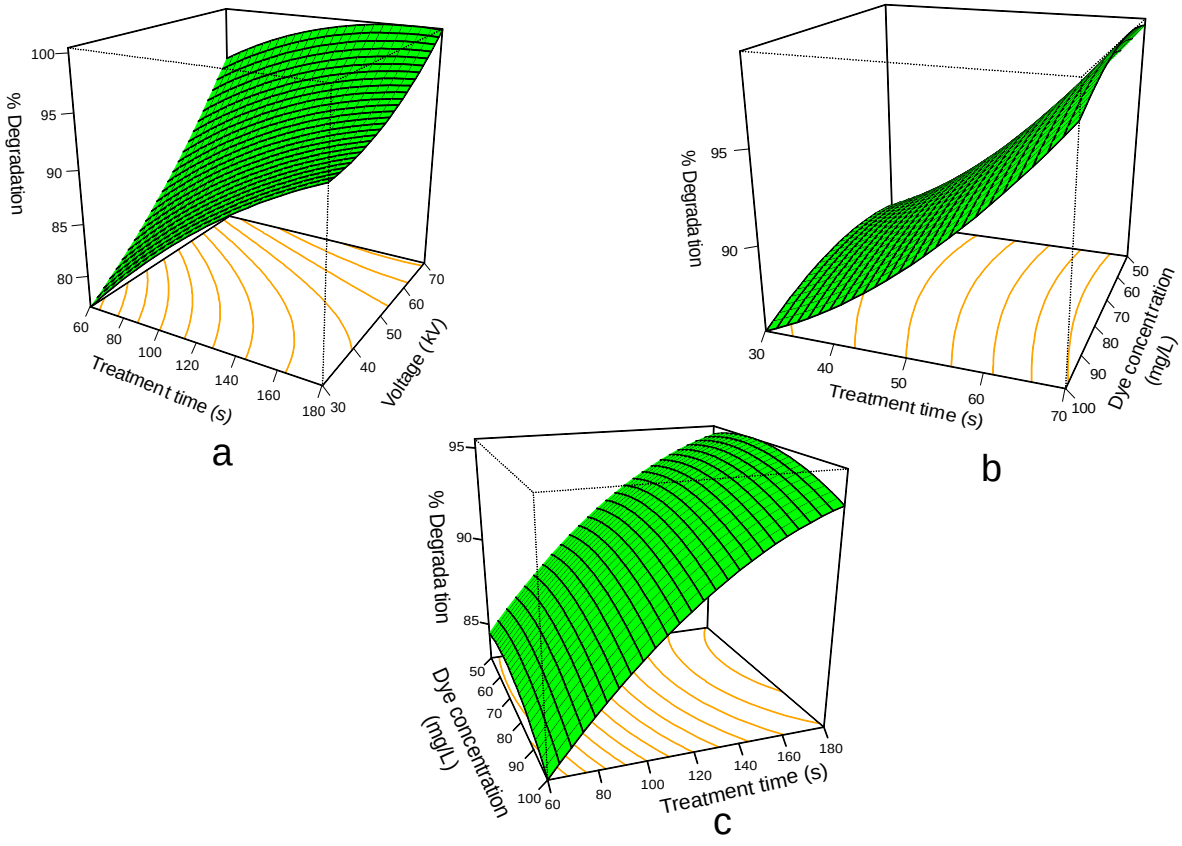


Fig.6. Surface plots for % degradation

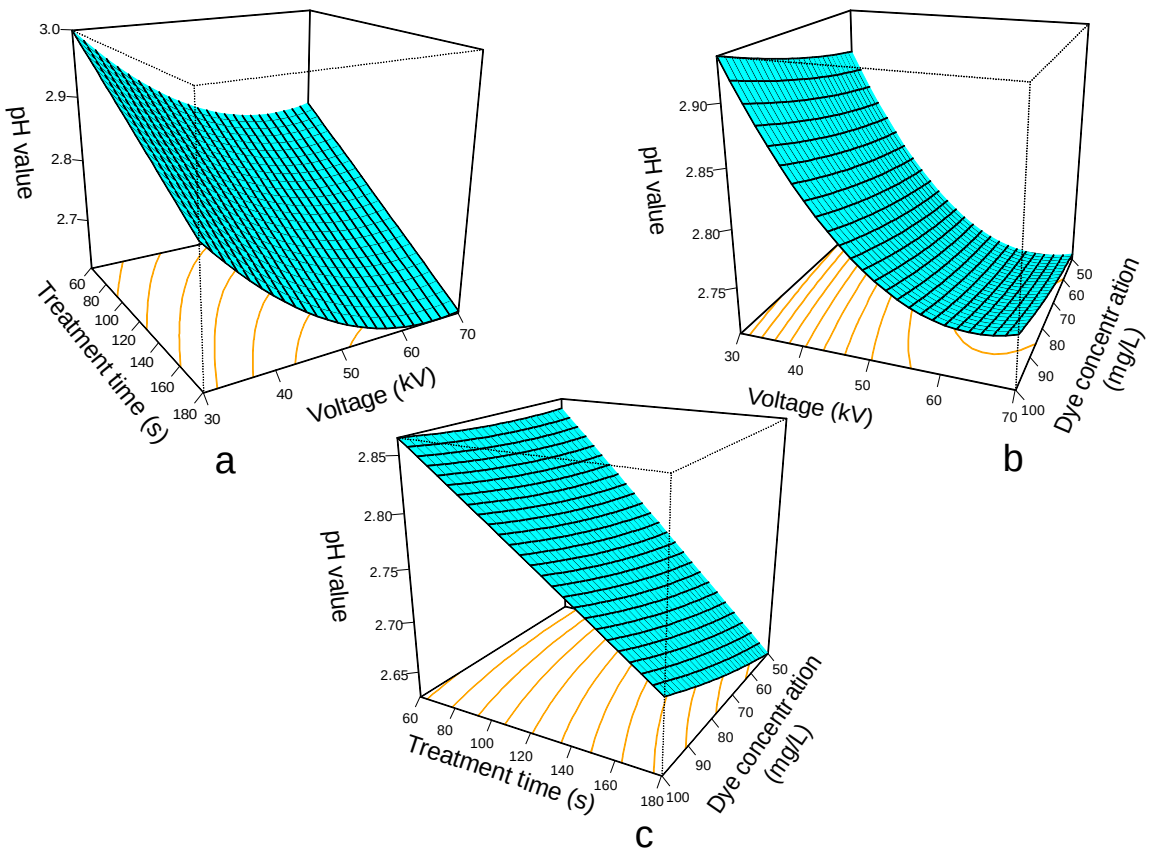
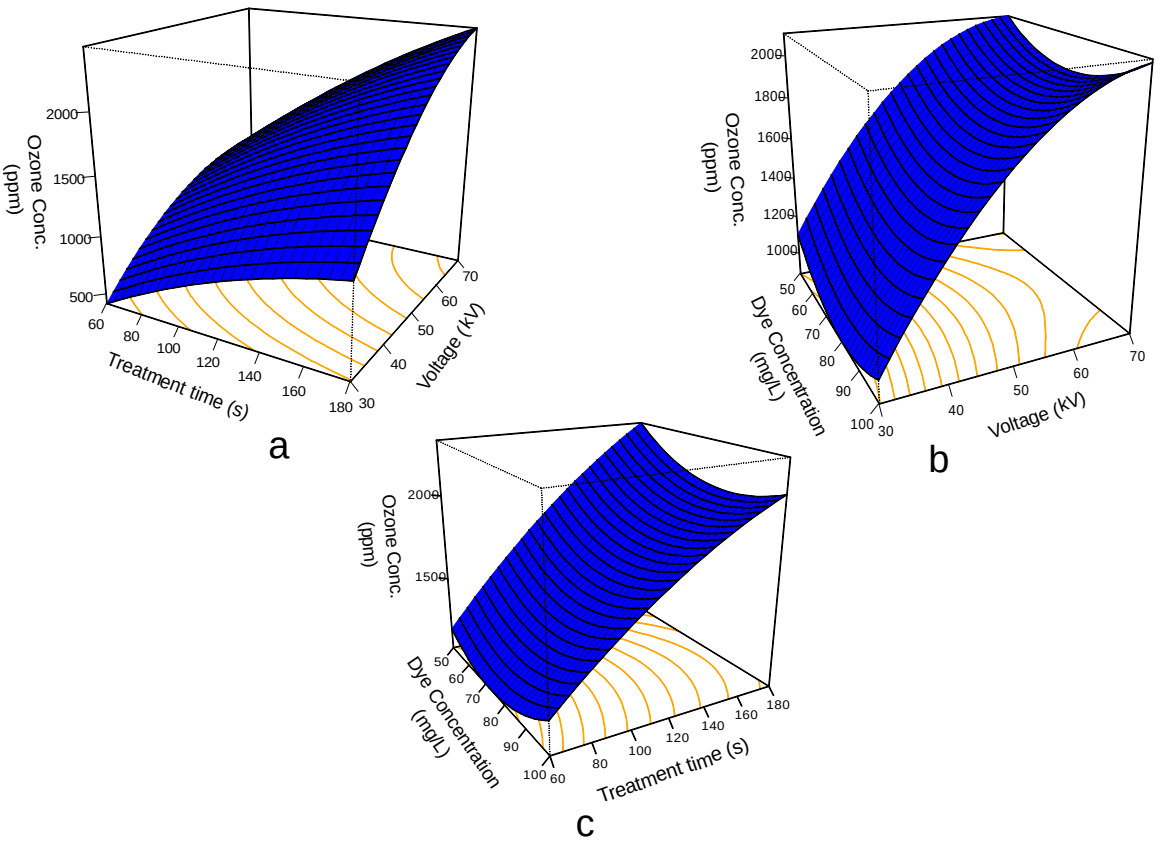


Fig.7. Surface plots for pH value



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402 **Fig.8.** Surface plots for ozone concentration

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Tables

Table 1

Independent factors and their coded levels

Independent factors	Symbol		Coded levels		
	Coded	Uncoded	-1	0	+1
Voltage (kV)	X_1	x_1	30	50	70
Time (Sec)	X_2	x_2	60	120	180
Dye Concentration(mg/L)	X_3	x_3	50	75	100

Table 2

The 3-factor Box Behnken design matrix.

Experiment no.	Variables (coded level)			Variables (actual level)		
	Voltage, X_1	Treatment time, X_2	Dye conc., X_3	Voltage, x_1 (kV)	Treatment time, x_2 (s)	Dye conc., x_3 (mg/L)
1	-1	-1	0	30	60	75
2	-1	0	+1	30	120	100
3	0	-1	-1	50	60	50
4	+1	0	-1	70	120	50
5	0	+1	-1	50	180	50
6	0	+1	+1	50	180	100
7	0	0	0	50	120	75
8	-1	+1	0	30	180	75
9	-1	0	-1	30	120	50
10	0	0	0	50	120	75
11	+1	+1	0	70	180	75
12	+1	-1	0	70	60	75
13	0	0	0	50	120	75
14	+1	0	+1	70	120	100
15	0	-1	+1	50	60	100

Variables x_1: Voltage, x_2: Treatment time, x_3: Dye concentration

Table 3

Response functions for the testing of atmospheric air plasma treated dye mixture

Experiment no.	Response functions		
	Experimental values		
	% degradation (%)	pH value	Ozone concentration (ppm)
1	78.365	3.02	500
2	85.0123	2.93	900
3	83.172	2.83	1200
4	99.5426	2.72	2200
5	96.125	2.64	2300
6	95.1253	2.72	2100
7	91.256	2.76	1600
8	92.523	2.8	1300
9	86.523	2.9	1000
10	91.253	2.71	1700
11	98.992	2.6	2400
12	96.243	2.86	1100
13	92.513	2.8	1650
14	97.956	2.75	2200
15	81.789	2.85	1250

Variables- x_1: Voltage, x_2: Treatment time, x_3: Dye concentration

Table 4

Coefficient of polynomials and corresponding t and p values from the data of Box bhenken design

Source of variation	% degradation		pH value		Ozone concentration	
	Coefficient of polynomial	t-value	Coefficient of polynomial	t-value	Coefficient of polynomial	t-value
Constant	91.674	100.626***	2.757	123.557***	1650.000	21.527***
x_1	6.289	11.272***	-0.090	-6.587**	525.000	11.185***
x_2	5.399	9.679***	-0.100	-7.319***	506.250	10.786***
x_3	-0.685	-1.229^{NS}	0.020	1.464^{NS}	-31.250	-0.666 ^{NS}
x_1^2	1.531	1.865 ^{NS}	0.064	3.191*	-231.250	-3.347*
x_2^2	-1.674	-2.039 ^{NS}	-0.083×10^{-2}	-0.042 ^{NS}	-93.750	-1.357 ^{NS}
x_3^2	-0.947	-1.153 ^{NS}	0.004	0.207 ^{NS}	156.250	2.262 ^{NS}
x_1x_2	-2.852	-3.615*	-0.01	-0.518 ^{NS}	125.000	1.883 ^{NS}
x_1x_3	-0.019	-0.024 ^{NS}	-1.180×10^{-16}	0.000 ^{NS}	25.000	0.377 ^{NS}
x_2x_3	0.096	0.122 ^{NS}	0.015	0.776 ^{NS}	-62.500	-0.942 ^{NS}
R^2	0.98***		0.96**		0.98***	

SE = standard error; * Significant at p≤0.05; ** Significant at p≤0.01; *** Significant at p≤0.001; **** Significant at p≤0.0001; ^{NS}not significant.

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